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THE EFFECT OF STRESS ON HYDRIDE PRECIPITATION, (U)

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THE EFFECT OF STRESS ON HYDRIDE PRECIPITATION

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Introduction

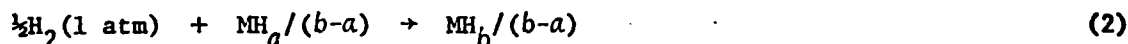
A major difficulty in comprehending the mechanism of stress induced hydride fracture (1,2) has been brought to the attention of one of the authors (HKB) by the other two. This difficulty has arisen because a clear distinction was not made between uniformly and non-uniformly stressed situations in the metal-hydrogen systems previously discussed (1,4). Since this distinction is a crucial one in understanding the proposed fracture mechanism, an attempt will be made here to resolve this difficulty. In addition, the discussion will encompass some general aspects of the effects of stress on hydride precipitation.

The Effect of a Uniform Stress on Hydride Precipitation

The hydride phase can be precipitated by cooling a closed system consisting of a solid solution of interstitially dissolved hydrogen. The hydrogen solubility, a , which coexists with the hydride phase at various temperatures constitute the solvus. An equation describing the solvus is given by

$$\ln a = \text{const.} - \Delta H_{\text{sol}}/RT \quad (1)$$

where ΔH_{sol} is known as the solvus enthalpy. Alternatively, the hydride phase can be precipitated in an open system by the addition of $\text{H}_2(\text{g})$ to the hydrogen-saturated solution, i.e.,



where b is the H-to-metal atom ratio in the hydride phase which coexists with the hydrogen-saturated solution. The equation analogous to equation 1 for reaction 2 is

$$\ln(p_{\text{H}_2}(\text{equil})/\text{atm})^{1/2} = \text{const.} - \Delta H(\frac{1}{2}\text{H}_2 + a \rightarrow b)/RT \quad (3)$$

where $\frac{1}{2}\text{H}_2 + a \rightarrow b$ represents reaction 2. The effect of a uniform stress on the thermodynamics of hydride precipitation will be considered for both cases for two types of metal-hydrogen systems. For one type V_{H} , the partial molar volume of hydrogen in the solid, is equal in the solid solution and hydride phases. In the other type, V_{H} may change in passing to the hydride phase. In this communication we will associate an invariance of V_{H} with miscibility gap systems such as Pd-H and Nb-H($\alpha \rightarrow \alpha'$), and a change in V_{H} upon hydride formation with structural transformation systems, e.g., Ti-H($\alpha \rightarrow \gamma$). Experimental evidence (6,7) suggests that the first case corresponds to miscibility gap systems and the second case to structural transformation systems i.e., in the first case the metallic matrix retains its symmetry upon hydride formation whereas

in the second case it does not.

The effect of a uniform stress on the solvus can be derived as follows: The change in relative chemical potential of hydrogen, $\Delta\mu_H = \mu_H - \frac{1}{2}\mu_{H_2}^\circ$ (1 atm), with stress, $-\sigma = p$, is given by

$$\left(\frac{d\Delta\mu_H}{dp}\right)_{\text{at } a} = \left(\frac{\partial\Delta\mu_H}{\partial p}\right)_a + \left(\frac{\partial\Delta\mu_H}{\partial a}\right)_p \left(\frac{da}{dp}\right) \quad (4)$$

The first term on the right-hand-side of equation 4 allows for the change of $\Delta\mu_H$ with stress at a fixed hydrogen content in the α -phase near the phase boundary. The second term allows for the change of $\Delta\mu_H$ as the phase boundary, a , changes with stress. Rearranging equation 4 gives equation 5

$$\left(\frac{da}{dp}\right) = \frac{\left(\frac{d\Delta\mu_H}{dp}\right)_{\text{at } a} - \left(\frac{\partial\Delta\mu_H}{\partial p}\right)_a}{\left(\frac{\partial\Delta\mu_H}{\partial a}\right)_p} \quad (5)$$

Since the relative chemical potential of dissolved hydrogen at a must have the same value and change in the same way with applied stress as the relative chemical potential for the two solid phase coexistence region, it follows that $\left(\frac{d\Delta\mu_H}{dp}\right)_{\text{at } a}$ must be identical to the same quantity for reaction 2. Therefore $\left(\frac{d\Delta\mu_H}{dp}\right)_{\text{at } a}$ can be determined from the volume change for reaction 2 as follows: The total volume V may be expressed as

$$V = n_H V_H + n_M V_M \quad (6)$$

where V_M is the partial molar volume of metal and n_H and n_M are number of mols of hydrogen and metal, respectively. It follows from equation 6 that

$$V/n_M = r V_H + V_M \quad (7)$$

where r is the H-to-metal atom ratio at any hydrogen concentration. The Gibbs-Duhem equation relating partial volumes (T and p constant) is

$$n_H dV_H + n_M dV_M = 0 \quad (8)$$

or

$$V_M = V_M^\circ + \int_0^r V_H dr - r V_H \quad (9)$$

where $V_M^\circ = V_M(r=0)$. Since for miscibility gap systems, V_H is assumed to be independent of r , equation 9 reduces to

$$V_M(r) = V_M^\circ \quad (10)$$

Using equations 6 and 10, the volume change for reaction 2 is

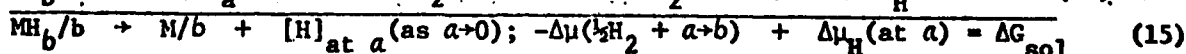
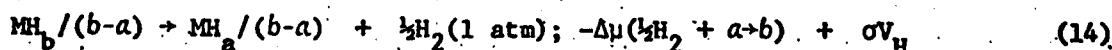
$$\Delta V = V_H - \frac{1}{2}V_{H_2} \quad (1 \text{ atm}) \quad (11)$$

The value of $\left(\frac{\partial\Delta\mu_H}{\partial p}\right)_a$, the second term in the numerator of equation 5, can be obtained from the volume change for the relative partial molar reaction



Using equation 6, the volume change for this reaction is also given by 11 and it follows that $(da/dp) = 0$ since the denominator of equation 5 is finite. The solvus concentration, a , is therefore unaffected by uniform stress for miscibility gap system.

The volume changes corresponding to the numerator of equation 5 are those for the reverse of reaction 2 plus reaction 12 and this sum represents the solvus reaction as $a \rightarrow 0$, i.e.,



and it can be seen again that the effect of the uniform stress cancels in the solvus reaction. Reaction 15 corresponds to the transfer of one mol of H from the hydride phase to the H-saturated solution (as $\alpha \rightarrow 0$) in keeping with the usual definition of the solvus reaction (8).

For a structural transformation system, e.g., $\alpha \rightarrow \beta$ (Nb-H), the solvus will be slightly affected by a uniform stress and this can be seen from a consideration of reactions 13-15. The volume change, for the solid phase of reaction 13, is $V_H^{\text{(solid solution)}}$ and for 14 (as $\alpha \rightarrow 0$) is $(V_M^{\circ} - V(\text{MH}_b))/b$ where $V(\text{MH}_b)$ is the molar volume of MH_b . We then obtain

$$\Delta G_{\text{sol}}^{\sigma > 0} = \Delta G_{\text{sol}}^{\sigma = 0} + \sigma \left[V_H + \frac{V_M^{\circ} - V(\text{MH}_b)}{b} \right] \quad (16)$$

If the hydride phase is an ordered one, e.g., $\alpha \rightarrow \beta$ (Nb-H), the volume change can be obtained by first considering the change to the disordered, miscibility gap hydride phase followed by an ordering of this phase, i.e., the volume change would be $\Delta V(\text{ordering of MH}_b/b)$. Peisl (7) has noted that the experimental volume changes of a large number of metal-H systems, both miscibility gap and structural transformation ones, can be derived by assuming that V_H and V_M are constants equal to their values in the solid solution with $V_H \sim 1.75 \text{ cm}^3 (\text{mol H})^{-1}$. Therefore the effect of a uniform stress on the solvus is expected to be generally minimal.

This section can be summarized by stating that the solvus is unaffected by a uniform stress if the volume change for the solvus reaction is zero because the stress cannot do work on the system. In practice the volume change is very small or zero and therefore we would expect only a small perturbation of the solvus by a uniform stress.

By contrast, a uniform stress will affect hydride precipitation when it occurs by reaction 2. For a miscibility gap system we obtain for reaction 2

$$\Delta \mu_H^{\sigma > 0} = \Delta \mu_H^{\sigma = 0} - \sigma V_H \quad (17)$$

For a structural transformation system the volume change to be used in equation 17 is $[V(\text{MH}_b) - (V_M^{\circ} + aV_H)]/(b-a)$.

The Effect of a Non-Uniform Stress on Hydride Precipitation

The mechanism of hydrogen embrittlement by stress induced hydride precipitation is based on the formation of a triaxial tensile stressed volume in front of the crack tip when an external stress is applied to the system. The hydride phase precipitates in this highly stressed volume and since the hydride phase is brittle, the crack propagates through the stress induced precipitate. The fracture proceeds by repeated hydride formation and fracture (2-4, 9-12). A thermodynamic discussion of this process has been presented based on the free energy changes which occur on hydride precipitation constrained by the solid solution. In the present communication we present an alternative discussion of unconstrained hydride precipitation under inhomogeneous stress which is consistent with the previous discussion of homogeneous stress.

Our thermodynamic model for this process is a small highly stressed volume at the crack tip which is thermodynamically linked to a reservoir of α phase solid solution which is much less stressed. We will assume this reservoir to be in a state of zero stress. This latter assumption and the assumption of a uniform stress in the volume in front of the crack is unrealistic but will be assumed for simplicity of presentation and will not affect the general conclusions. As previously discussed, the solvus is unchanged within the highly stressed volume (Fig. 1). However, within the tensile stressed volume the chemical potential of hydrogen is reduced relative to the surrounding unstressed α phase by $-\sigma V_H$ (Fig. 1). The hydride phase can precipitate in the stressed volume when the chemical potential of hydrogen in the unstressed α solid solution is equal to or greater than that of the hydride which coexists with the saturated solid solution in the stressed volume, i.e., when the unstressed volume reservoir has a hydrogen concentration $r > a'$ (Fig. 1). Thus the solvus of the unstressed reservoir is a' while within the stressed volume it is unchanged at a (Fig. 1). The appropriate solvus reaction (as $a, a' \rightarrow 0$) is



where $[\text{H}]_{a'}^{\sigma = 0}$ represents one mol of hydrogen dissolved in the unstressed α reservoir at $r = a'$. For this process it can be shown from consideration of reactions 13 (unstressed) and 14 (stressed) that

$$\ln a' = \text{constant} - \Delta H_{\text{sol}}/RT - \sigma V_H/RT \quad (19)$$

for a miscibility gap system. In the case of a structural transformation system the appropriate volume term is $(V(MH_b) - (V_M + aV_H))/(b-a)$. The units of ΔH_{sol} and σV_H are energy per mol H. It is the effect of stress on the solvus given by equation 19 (which was expressed in a different but equivalent form) which was previously employed (1-4) without explicitly stating that it applied only in the presence of an inhomogeneous stress.

A source of possible confusion is that there are now two "solvus" values: a (unchanged by stress) in the volume where the high stress exists and a' (changed by stress) in the relatively unstressed reservoir (Fig. 1).

In practice the solid solution surrounding the crack tip will not be expected to be at $r=a'$ but at an r value, $a > r > a'$ and the system will not necessarily be at equilibrium. The hydrogen flux to the crack tip will not markedly reduce the concentration in the reservoir if it is sufficiently extensive and the highly stressed volume is small. Hence $\mu_H(\text{reservoir}, \sigma=0)$ will remain larger than $\mu_H(\sigma>0)$ in the small stressed volume in front of the crack unless this latter volume is fully converted to the hydride phase and further hydrogen added to the hydride phase until the chemical potentials are equal. Before this occurs, the crack will propagate through the hydride and the process will be repeated. Alternatively the formation of the hydride with the attendant increase in volume at the crack tip will reduce the local stress field until the chemical potentials are equal.

With regard to hydride precipitation via reaction 2, an inhomogeneous tensile stress will cause hydride precipitation in the stressed regions when the chemical potential of dissolved hydrogen reaches that shown by the dashed horizontal line (Fig. 1). The hydride phase will form in these regions and further hydrogen will dissolve in this hydride phase before hydride starts to precipitate in the unstressed part of the sample. This can have practical consequences for samples which have been cycled through the phase change and the hydrogen removed without a high temperature anneal. This treatment gives rise to cracks and consequently small tensile stressed regions. Experimental evidence has been recently given which suggests that hydride phase can form in palladium samples, which have been cycled through the phase change, before the normal equilibrium absorption pressure is reached (13).

Pardee and Paton (14) have recently discussed hydrogen diffusion and solubility in an elastoplastic field arising from formation of titanium hydride in α -titanium and their paper should be consulted especially with respect to the effects of stress on structural transformation systems.

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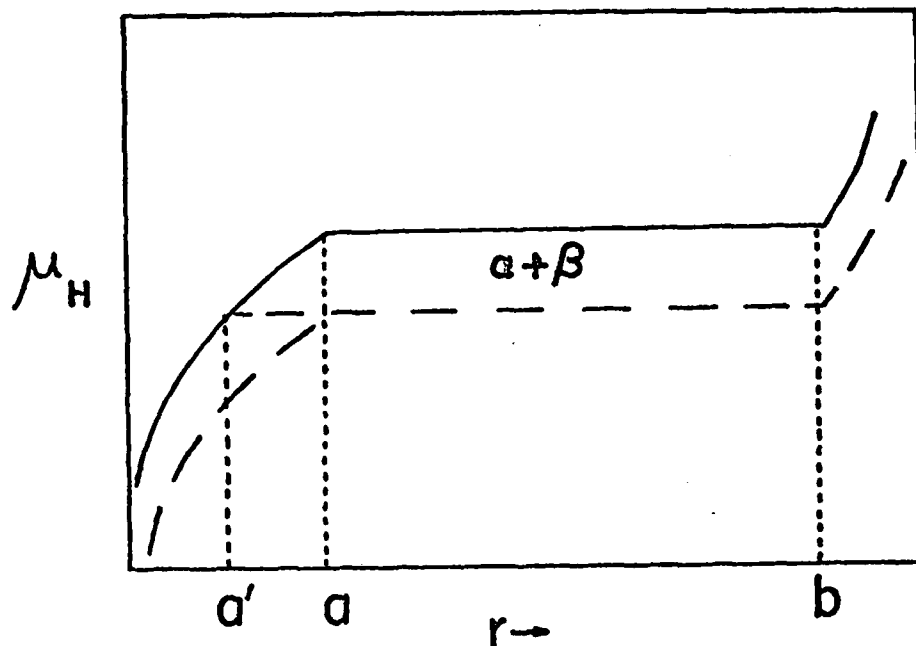


FIG. 1

The effect of stress on the chemical potential of hydrogen. ———, zero stress; — — — —, uniform tensile stress. Both curves refer to the chemical potentials for hydride formation; a similar set of curves would be obtained for hydride decomposition but due to hysteresis the two phase coexistence regions would be at lower values of μ_H .

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